

DTIC FILE COPY

2

AD-A223 632

OFFICE OF NAVAL RESEARCH
TECHNICAL REPORT

FOR

Contract N00014-88K-0369

R&T Code 4133025

Technical Report No. 5

Accession For	
NTIS GRA&I	<input checked="checked" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution/	
Availability Codes	
Dist	Avail and/or Special

A-1



Sym-cis-Dioxo(2,2'-bipyridine)bis(pyridine)rhenium(V)

Hexafluorophosphate, *Sym-cis*-[(O)₂Re(bpy)(py)₂](PF₆)

by

M. S. Ram and Joseph T. Hupp

Department of Chemistry
Northwestern University
Evanston, IL 60208-3113

DTIC
JUN 1990
G

Reproduction in whole, or in part, is permitted for any purpose of the United States Government.

This document has been approved for release and sale: its distribution is unlimited

90 07 3 205

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION		1b. RESTRICTIVE MARKINGS	
2a. SECURITY CLASSIFICATION AUTHORITY		3. DISTRIBUTION/AVAILABILITY OF REPORT	
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE			
4. PERFORMING ORGANIZATION REPORT NUMBER(S) 05		5. MONITORING ORGANIZATION REPORT NUMBER(S)	
6a. NAME OF PERFORMING ORGANIZATION Northwestern University	6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION	
6c. ADDRESS (City, State and ZIP Code) Department of Chemistry Evanston, IL 60208-3113		7b. ADDRESS (City, State and ZIP Code)	
8a. NAME OF FUNDING/SPONSORING ORGANIZATION Office of Naval Research	8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER	
8c. ADDRESS (City, State and ZIP Code) Department of the Navy Arlington, Virginia 22217		10. SOURCE OF FUNDING NOS.	
		PROGRAM ELEMENT NO.	PROJECT NO.
		TASK NO.	WORK UNIT NO.
11. TITLE (Include Security Classification) Sym-cis-Dioxo(2,2'-bipyridine)bis(pyridine)...			
12. PERSONAL AUTHOR(S) M. S. Ram and Joseph T. Hupp			
13a. TYPE OF REPORT Technical Report	13b. TIME COVERED FROM _____ TO _____	14. DATE OF REPORT (Yr., Mo., Day) 6/27/90	15. PAGE COUNT 6
16. SUPPLEMENTARY NOTATION <i>(Dioxo(2,2'-bipyridine)bis(pyridine)rhenium(V))</i>			
17. COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
FIELD	GROUP	SUB. GR.	
		Hexafluorophosphates, Ligands, synthesis, Pyridyl complex, bpy, py (JG)	
19. ABSTRACT (Continue on reverse if necessary and identify by block number) (Deuterium)			
<p>The complex sym-cis-(bpy)(py)₂Re(O)₂ has recently been synthesized¹ and its structure has been determined. The complex represents the first confirmed hexacoordinate cis-dioxo complex of rhenium and is one of only a handful of d⁵ metal complexes known to possess the cis-dioxo ligand configuration. The dioxo complexes of rhenium(V) are of interest in general because of their multielectron electrochemical behavior, persistent (in some instances) photophysical activity, and possible redox catalytic activity. The unusual geometry for the (bpy)(py)₂Re(O)₂⁺ species exerts a profound influence upon all of these properties. We report here an improved procedure for its synthesis. The method appears to be general for synthesizing various substituted pyridyl and bipyridyl complexes. (The earlier method¹ was notably deficient in this respect.) The new synthesis also represents a considerable savings in total time and in effort needed to achieve purification. The current synthesis can be considered complementary to the synthesis of trans-terakis(pyridine)dioxorhenium(V) and trans-bis(ethylenediamine)dioxorhenium(V) complexes which have been previously described in Inorganic Synthesis.^{10,11}</p>			
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT. <input type="checkbox"/> OTIC USERS <input type="checkbox"/>		21. ABSTRACT SECURITY CLASSIFICATION	
22a. NAME OF RESPONSIBLE INDIVIDUAL Joseph T. Hupp		22b. TELEPHONE NUMBER (Include Area Code) (708) 491-3504	22c. OFFICE SYMBOL

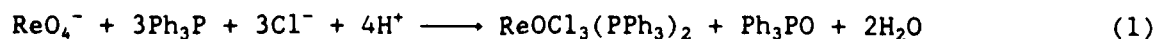
Introduction

The complex *sym-cis*-(bpy)(py)₂Re(O)₂⁺ has recently been synthesized¹ and its structure has been determined.² The complex represents the first confirmed hexacoordinate *cis*-dioxo complex of rhenium and is one of only a handful of d² metal complexes known to possess the *cis*-dioxo ligand configuration.³⁻⁵ The dioxo complexes of rhenium(V) are of interest in general because of their multielectron electrochemical behavior,^{1,6} persistent (in some instances) photophysical activity,⁷⁻⁹ and possible redox catalytic activity.^{6,9} The unusual geometry for the (bpy)(py)₂Re(O)₂⁺ species exerts a profound influence upon all of these properties. We report here an improved procedure for its synthesis. The method appears to be general for synthesizing various substituted pyridyl and bipyridyl complexes. (The earlier method¹ was notably deficient in this respect.) The new synthesis also represents a considerable savings in total time and in effort needed to achieve purification. The current synthesis can be considered complementary to the synthesis of *trans*-terakis(pyridine)dioxorhenium(V) and *trans*-bis(ethylenediamine)dioxorhenium(V) complexes which have been previously described in Inorganic Synthesis.^{10,11}

Procedure

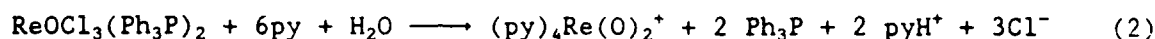
The total time required for the synthesis is ~two days. For steps 4 and 5 (only) the time required is about 3 hours. The net yield of the purified complex (steps 1-5) is ~15%.

Step 1. Synthesis of ReOCl₃(PPh₃)₂



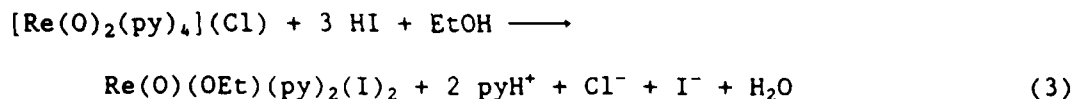
The complex was prepared by the method described by Wilkinson, et al.¹² (To a boiling solution of 10 g perrhenic acid plus 10 ml of concentrated HCl in 100 ml ethanol was added 50 g triphenylphosphine (Ph₃P) dissolved in 150 ml refluxing ethanol. The mixture was boiled for three minutes (with swirling), cooled to about 50° C and filtered. The complex was thoroughly washed with toluene and dried.) The green product was used without purification.

Step 2. Synthesis of *trans*-[(py)₄Re(O)₂](Cl)



Although there are other methods of synthesis for this complex^{10,12-14}, we find the following method, a *modification* of Wilkinson's procedure,¹² the most convenient. 6 g of ReOCl₃(PPh₃)₂ was mixed with 12 ml pyridine and 6 ml water in 120 ml acetone. The mixture was refluxed for 90 minutes and cooled in ice-water for 30 minutes. The orange yellow complex (which precipitates even while refluxing) is collected by filtration (porous glass frit), washed with two 20 ml portions of toluene and two 20 ml portions of ether. Yield 3.7 g (90%). In our hands this procedure proved to be superior (with respect to time and yields) to those described in references 10 and 12.

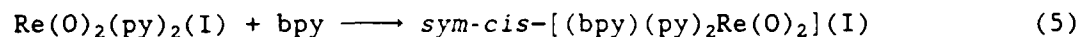
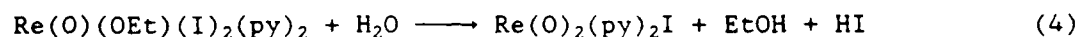
Step 3. Synthesis of Re(O)(OEt)(I)₂(py₃P)₂



This complex is prepared according to a literature method,¹⁴ but again with a slight modification. 2.0 g of *trans*-[(py)₄Re(O)₂](Cl) was dissolved in 60 ml of refluxing ethanol. 3 ml of 57% HI was added to the solution. The

mixture was then refluxed with stirring for 15 minutes followed by cooling in ice water for 45 minutes. The precipitated green complex was collected by filtration, washed with three 20 ml portions of ethanol and dried. Yield 1.16 g (50%)

Step 4. Synthesis of *sym-cis*-[(bpy)(py)₂Re(O)₂](I)



1.15 g (1.7 mmol) of the green complex obtained in step 3 was mixed with 2.6 g (~17 mmol) of 2,2'-bipyridine (bpy) and 2 ml water in 60 ml acetone. The mixture was stirred at room temperature for 1 h, and then rotary evaporated (at 35° C) until the volume was 10 ml. To complete the precipitation of the complex, 200 ml of ether was added (with stirring). The purple black solid was filtered with a medium porosity frit and washed with 2 x 10 ml portions of ether. Yield 0.85 g (73%)

Step 5. Synthesis of *sym-cis*-[(bpy)(py)₂Re(O)₂](PF₆)

0.85 g of the iodide salt of the complex was dissolved in 130 ml water (ultrasonication dissolved most of the complex). 5 ml of a saturated aqueous solution of NH₄PF₆ was then added to precipitate the *sym-cis*-[(bpy)(py)₂Re(O)₂](PF₆). (The addition of 10 ml of saturated NaClO₄ solution likewise gives the crude *sym-cis*-[(bpy)(py)₂Re(O)₂](ClO₄) salt. The perchlorate salt is advantageous because of its relatively high aqueous solubility. The purification of this material follows the same procedure as for the PF₆⁻ salt.)

CAUTION: *Perchlorates of heavy metal ions with organic ligands are potentially explosive. It is advisable to handle or store < 50 mg of this material, and then also with the usual precautions to avoid mixing with concentrated acids or EtOH. Furthermore, it should not be subjected to mechanical or thermal stress.*

The complex was collected on a medium glass frit, washed with 2 x 2 ml water and with 2 x 10 ml of ether containing 10% acetone. Crude yield 0.5 g (57%). The complex is easily purified by adsorbing onto a Brockmann I, neutral alumina (Aldrich) column (about 30 ml volume) containing CH₂Cl₂ as solvent. Elution of the desired purple band is accomplished with 30% 2-propanol/70% CH₂Cl₂ solution. The complex is precipitated from the eluent solution by addition of 200 ml ether (with stirring), then filtered with a medium frit and washed with 2 x 10 ml portions of ether containing 10% acetone. The solid is dried at -40° C in a vacuum oven overnight. Yield 0.35 g (70%); Analysis: Found: C 35.1%, H 2.72%, N 8.05%; Calc: C 35.4%, H 2.65%, N 8.26%.

Properties

The *sym-cis*-[(bpy)(py)₂Re(O)₂]⁺ complex is burgundy red in color. The perchlorate salt is fairly highly soluble in water (~5 mM) as is the iodide. (The iodide salt is not particularly useful, however, for oxidative electrochemical studies). Both the perchlorate and the hexafluorophosphate salts are highly soluble in polar organic solvents. The complex decomposes significantly (~10%) in two hours in water and more slowly in other solvents. With excess pyridine in acetonitrile as solvent, it rapidly reverts to *trans*-tetrakis(pyridine)dioxorhenium(V). The complex has a solvent-dependent

electronic absorption spectrum. In water four absorption maxima (ϵ , $M^{-1} \text{ cm}^{-1}$) are seen: 498 nm (4.2×10^3), 383 nm (8.3×10^3), 300 nm (1.64×10^4) and 245 nm (1.45×10^4). In acetonitrile the two longer wavelength transitions move to 527 nm and 406 nm. Symmetric and asymmetric O=Re=O stretches were observed by both IR and resonance Raman at $845 \text{ cm}^{-1}(s)$ and $906 \text{ cm}^{-1}(s)$. The δ values (in ppm with respect to $\text{CD}_3\text{COCHD}_2$ at 2.04 ppm as reference) for the proton magnetic resonances are as follows: 10.87 (d, 2H), 8.70 (d, 2H), 8.44 (d, 4H), 7.99 (t, 2H), 7.88 (t, 2H), 7.69 (m, 6H). The electrochemical behavior is quite distinctive. At pH 7 in water, a reversible oxidation to Re(VI) occurs at 0.63 V (vs. SCE). A quasi-reversible V/III couple exists at -0.63 V with a III/II couple at -0.91 V. At pH 13, the VI/V potential is unchanged. The reductive processes coalesce, however, to give an unusual three electron transformation (V/II) at -0.98 V.

References

1. Ram, M. S.; Johnson, C. J.; Blackbourn, R.; Hupp, J. T. Inorg. Chem., 1990, 29, 238.
2. Blackbourn, R.; Jones, L. M.; Ram, M. S.; Sabat, M.; Hupp, J. T. Inorg. Chem., 1990, 29, 1791.
3. Behling, T.; Cappanelli, M. V.; Skapski, A. J.; Wilkinson, G.; Polyhedron, 1982, 1, 840.
4. Dobson, J. C.; Takeuchi, K. J.; Pipes, D. W.; Geselowitz, D. A.; Meyer, T. J. Inorg. Chem., '986, 25, 2357.
5. Dobbson, J. C.; Meyer, T. J. Inorg. Chem., 1988, 27, 3283.
6. Pipes, D. W.; Meyer, T. J. Inorg. Chem., 1986, 25, 2357.
7. Winkler, J. R.; Gray, H. B. J. Am. Chem. Soc., 1983, 105, 1373.

8. Winkler, J. R.; Gray, H. B. Inorg. Chem., 1985, 24, 346.
9. Thorp, H. H.; Van Houten, J.; Gray, H. B. Inorg. Chem., 1989, 28, 889.
10. Chakravorti, M. C. Inorg. Synth., 1982, 21, 116.
11. Murmann, R. K.; Inorg. Synth., 1966, 8, 173.
12. Johnson, N. P.; Lock, C. J.; Wilkinson, G. J. Chem. Soc., 1964, 1064.
13. Brewer, J. C., Gray, H. B. Inorg. Chem., 28, 3334.
14. Freni, M.; Giusto, D.; Romiti, P.; Minghetti, G. Gazz. Chim. Ital., 1969, 99, 286.